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Preparation of a Perylenebisimide Acceptor with Serinol and Nonadecyl-Swallowtail Imides for Use in Molecular Rectification

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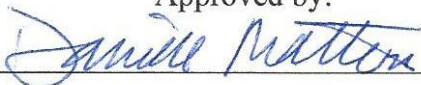
Tarrah Frederick

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of
the requirements of the Sally McDonnell Barksdale Honors College.

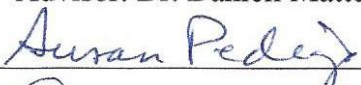
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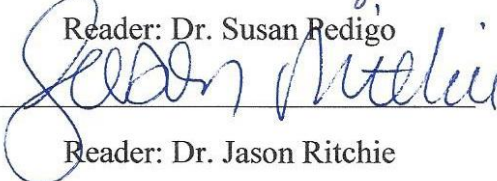
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Acknowledgments

I would like to take the time to acknowledge everyone who has helped me throughout my undergraduate research. I would like to thank my advisor, Dr. Daniell Mattern, for essentially teaching me everything that I know about organic chemistry and for always being available to explain even the simplest of concepts to me. I would also like to thank Dr. Mattern for the incredible opportunity to be a part of this lab. I also want to thank Dr. Trey Vaughan for taking the time to teach me the many lab techniques that I have used throughout the past few years and for helping me to discern my surplus of NMR spectra.

ABSTRACT

Several attempts were made to add 2-amino-1,3-propanediol to the acceptor perylene monoanhydride (PMA). The theoretical product, *N*-(10-nonadecyl)-*N'*-(1,3-dihydroxypropan-2-yl)perylen-3,4,9,10-bis(dicarboximide), is intended for use in unimolecular rectification because the perylenebisimide core is classified as a good acceptor due to its high electron affinity. Rectification usually utilizes donor- σ -acceptor molecules, whose localized orbitals permit electron transfer when placed between metal electrodes of asymmetric voltages. However, according to an “asymmetric rectification” analysis, an electron can pass from one electrode, through the LUMO of the acceptor, and then to the other electrode when said electrodes are held at certain voltages, and result in rectification if the acceptor is closer to one electrode than to the other.¹²

Electrical properties are typically measured on a monolayer of rectifying molecules. The desired perylenebisimide (PBI) must be amphiphilic in order to successfully form a monolayer to be used in Langmuir–Blodgett deposition, so that when deposited on a water layer, the molecules will arrange vertically, with the hydrophilic moiety going into the water and the hydrophobic moiety facing upward. Therefore, hydrophilic serinol and a hydrophobic nonadecyl swallowtail were used to achieve such amphiphilic properties when attached to the two ends of PBI.

Several difficulties arose from the reactions used to synthesize the PBI, such as unknown impurities, even after purification via column chromatography; potential by-products; non-planar orientations, which could have affected ¹H-NMR spectra; and intramolecular interactions. It is unclear why some of the reactions, though published in literature, were unsuccessful.

Nevertheless, the reactions and results discussed in this text are useful for devising methods for further efforts to synthesize the target PBI.

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List of Abbreviations and Symbols

aq.	aqueous
CDCl ₃	deuterated chloroform
COSY	Correlation spectroscopy
Δ	heat
D- σ -A	donor-sigma-acceptor
DCM	dichloromethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
eq.	equivalent
g	gram(s)
h	hour(s)
mg	milligram(s)
mL	milliliter
NMR	nuclear magnetic resonance
<i>p</i>	para
PBI	perylenebisimide
%	percent

PMA	perylene monoanhydride
PTCDA	perylene-3,4,9,10-tetracarboxylic dianhydride
sat.	saturated
TBDMSCl	<i>tert</i> -butyldimethylsilyl chloride
THF	tetrahydrofuran
TLC	thin layer chromatography
TsOH	<i>p</i> -toluenesulfonic acid or tosic acid

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I. Introduction

1.1 Aviram–Ratner Rectification

In 1974, Ari Aviram and Mark Ratner proposed that an electric current could be passed preferentially in one direction through an organic molecule.¹ This concept, known as unimolecular rectification, utilizes a set of compounds known as donor- σ -acceptor molecules. Accordingly, these molecules consist of an acceptor and a donor, which are connected covalently by a saturated sigma bridge (i.e. bond) that hinders localized donor-acceptor molecular orbital interaction.² A good acceptor ideally has a high first electron affinity, which means that the moiety is more likely to acquire an electron because such acquirement results in a decrease in, or release of, energy. The electron is, hence, acquired via an exothermic reaction, which is energetically favorable and makes the moiety a good electron acceptor. A good donor, on the other hand, ideally has a lower electron affinity but a lower first ionization potential, meaning that the energy required to gain an electron is high but to lose or donate an electron is low and, consequently, favorable. The acceptor has low-energy molecular orbitals, while the donor has high-energy orbitals (**Figure 1.1.1**). The sigma bridge, whose function is to decouple the donor from the acceptor and to minimize orbital overlap, was originally proposed as consisting of linked methylene groups. However, another method commonly used to decouple the donor from the acceptor is to use an unsaturated π vinyl bond that results in a dihedral twist of the donor relative to the acceptor, which results in minimized orbital overlap.^{2,3,4}

When placed as a monolayer between two electrodes, the D- σ -A molecules can exhibit rectification when a specific electrical bias is applied (i.e. when the voltage of one electrode is manipulated to differ from the other). In general, such bias makes electron flow possible because it causes the acceptor's LUMO and the donor's HOMO to fall between the Fermi levels

of the electrodes, and, under a sufficient amount of electrical bias, can cause electrons to preferentially flow in one direction, or rectify.

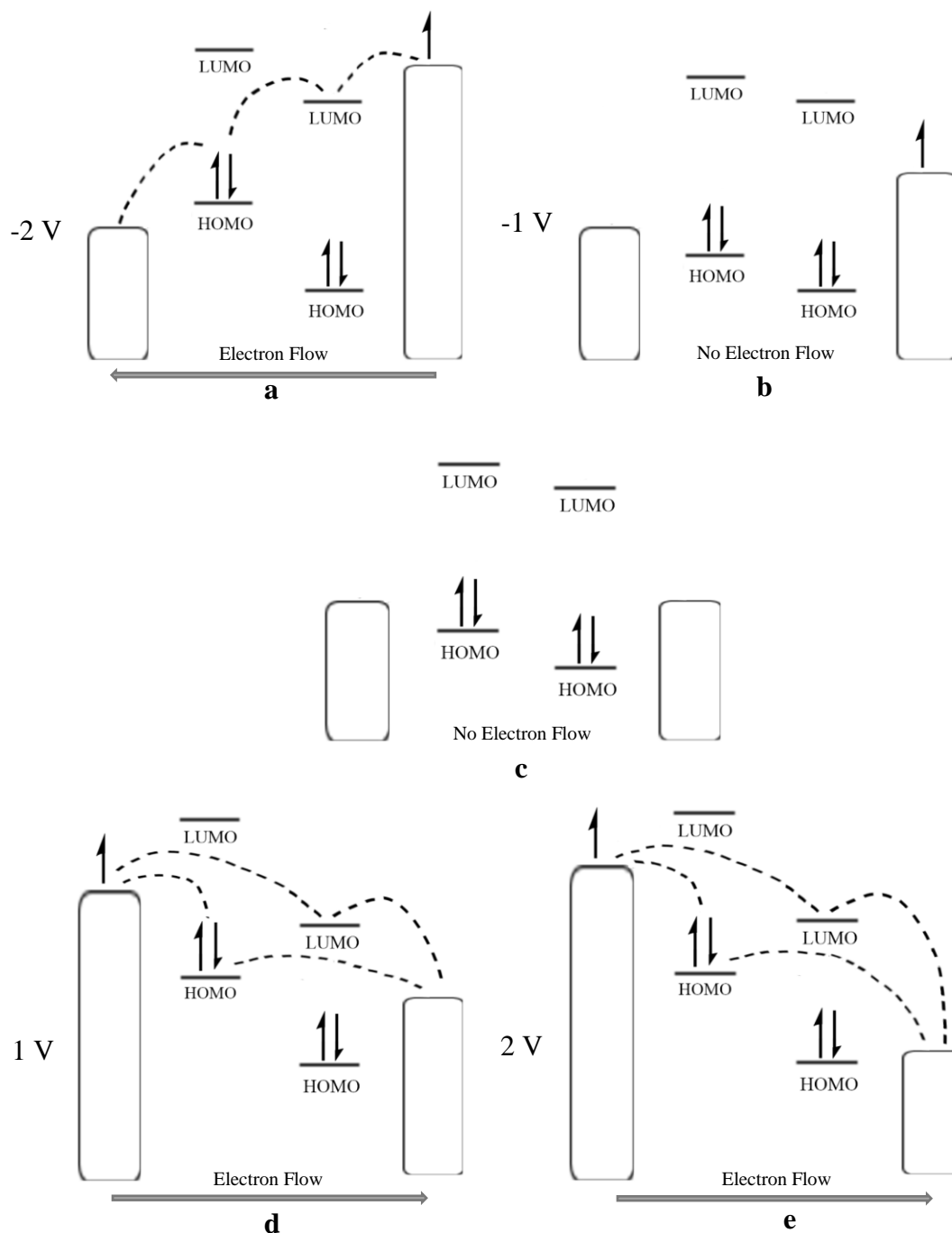


Figure 1.1.1: Proposed electron flow through D-σ-A molecules at (a) -2 V, (b) -1 V, (c) 0 V, (d) 1 V, and (e) 2 V biases.

Therefore, for Aviram–Ratner rectification, the electrodes' voltages are manipulated so that the Fermi level of the electrode nearest the acceptor is higher than the acceptor's LUMO and the Fermi level of the electrode nearest the donor is lower than the donor's HOMO.⁵ As this mode of rectification proposes, an electron can pass from the cathode, through the acceptor and donor, and then to the anode. As the above figure shows, a -2 V bias between the electrodes is needed for electrons to flow in the Aviram–Ratner direction (**a**).⁴ However, if the voltage difference is not great enough for the orbitals to fall within the energy gap, no flow will occur. As a result, no electron flow occurs at biases of -1 V (**b**) and 0 V (**c**).

Aviram–Ratner rectification is possible due to the differences in energy between localized orbitals of the donor and acceptor. For example, a current is possible from acceptor to donor when the LUMO of the acceptor is at a higher energy level than the HOMO of the donor.⁶ When placed between the electrodes, the D- σ -A molecule can, through resonant transfer, become an excited zwitterion, D⁺- σ -A⁻. The molecule can then, if within the energy gap between the Fermi levels of the electrodes, undergo an inelastic intramolecular electron transfer, returning to D⁰- σ -A⁰, resulting in an electron passing downhill from the cathode to the anode (Aviram-Ratner rectification).⁶

1.2 Anti–Aviram–Ratner Rectification

Contrary to Aviram and Ratner's theory, in some molecules, the electrons can travel through two possible pathways when a 1 V (**d**) or even 2 V (**e**) bias is applied, that is, in an anti–Aviram–Ratner direction.³ In this mode of current flow, the electrons can pass either through the HOMO of the donor to the other electrode or through the LUMO of the acceptor to the other electrode.

Usually, for this mode of current flow to occur, there must be an electrical bias between the electrodes such that the voltage of the electrode beside the donor is increased. This increase in voltage raises the electrode's Fermi level, causing the HOMO of the donor and the LUMO of the acceptor to now fall within the energy gap between the Fermi levels of the electrodes, allowing current flow. With this electrical bias, the electrons can then move through both pathways, constituting a two-way anti-Aviram-Ratner mode of current flow. As stated earlier, this two-way current flow occurs at both 1 V (**d**) and 2 V (**e**) biases, while electron flow in the Aviram-Ratner direction occurs only at a bias of -2 V (**a**). Since a current flows under a 1 V bias (**d**) and not a -1 V bias (**b**), the molecule exhibits anti-Aviram-Ratner rectification at 1 V, which many D- σ -A molecules have exhibited experimentally.⁷ Conversely, though electron flow is observed in both the -2 V and the 2 V biases, flow at -2 V bias is favored due to the electron having the ability to pass through both the donor and acceptor molecules, instead of just one or the other, providing a route with shorter tunneling distances. Therefore, at -2 V bias, the molecule exhibits Aviram-Ratner rectification. Some molecules have been shown to rectify in either direction, depending on the bias applied. Coined the Janus Effect by M.S. Johnson, et al., in 2014, these molecules exhibit anti-Aviram-Ratner rectification when exposed to 1 V bias yet exhibit Aviram-Ratner rectification when the bias is manipulated to -2 V.⁸

Additional factors also influence whether or not the orbitals will fall within the energy gap of the electrodes. It has been discovered that the LUMO of the acceptor and the HOMO of the donor vary in energy with the voltage applied and are somewhat proportional to the Fermi levels of their nearest electrode, specifically when Au is used.⁴ Due to these discoveries and to the reality of the two-way mode of rectification, it has been proposed that electron flow might be possible using only an acceptor molecule that is placed asymmetrically between the electrodes,

given sufficient electrical bias is applied (**Figure 1.2.1**). Theoretically, an electron current should flow in both directions. Since the same amount of electron flow would occur at -2 V and 2 V bias, no rectification should occur. However, rectification could occur at 1 V bias in the anti-Avram-Ratner direction, since no current should flow at -1 V bias.

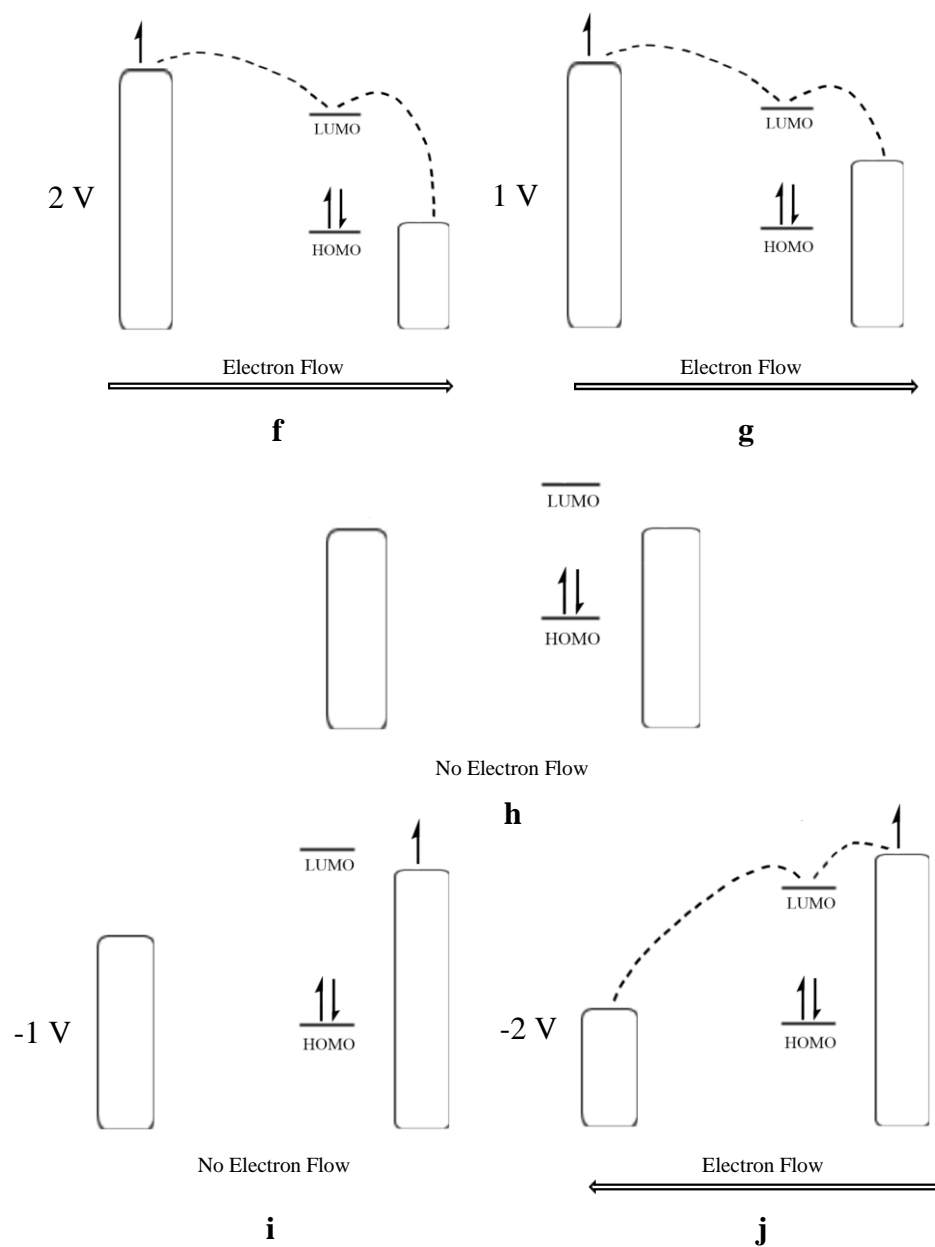


Figure 1.2.1: Molecular rectification through a perylenebisimide acceptor. **(f, g)** An electron current should theoretically flow at both 1 V and 2 V bias. **(h)** No current should occur. **(i, j)** A current should also occur in the other direction at -2 V but not at -1 V biases. Because the acceptor is closer to one electrode, its energy is more strongly affected by that electrode's voltage. The acceptor LUMO can move down into the energy gap in **(g)** under 1 V bias, but stays above the gap in **(i)** under -1 V bias.

1.3 Langmuir–Blodgett Method

In order to test whether or not an electric current will pass through the D- σ -A molecule, the molecules can be aligned as a monolayer, with each in the same orientation. To create this monolayer, the Langmuir-Blodgett (LB) technique is used. After Lord Rayleigh found that the thickness of a water-insoluble film can be calculated when deposited on a water layer, Agnes Pockels showed that the surface area of those films could be manipulated with barriers.³ Expanding on these discoveries, Irving Langmuir and Katherine Blodgett discovered what is known as the LB deposition process.

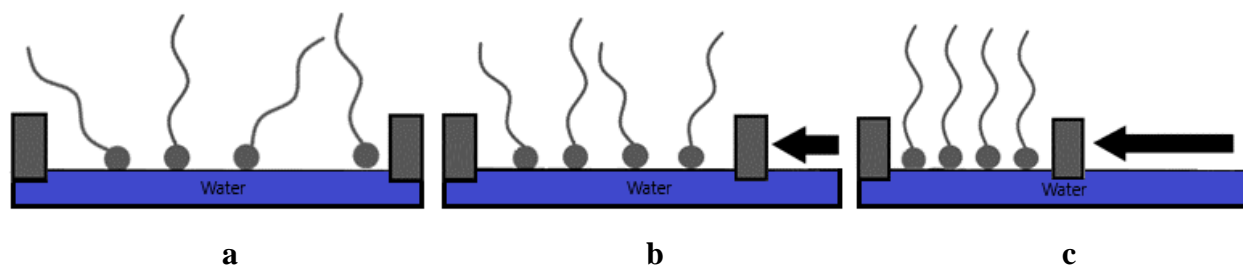


Figure 1.3.1: Monolayer in LB trough when **a)** not compressed, **b)** semi-compressed, and **c)** compressed.

For this technique, amphiphilic compounds, such as the D- σ -A molecules, are deposited on an aqueous layer in an LB trough. The hydrophilic moiety will then go into the water, while the hydrophobic end will come out of the water, causing the molecules to arrange vertically. The LB trough then compresses the molecules together (**Figure 1.3.1**). Dipping or removal of the electrode through the interface results in a monolayer deposited on the electrode, and repetitive dipping results in multilayers.⁹

1.4 Perylenebisimide as an Acceptor

The use of perylene-4,5,9,10-bis(dicarboximide) (PTCDA) as an acceptor in molecular rectification has been proposed due to its four carbonyl (C=O) groups, which make it a good acceptor. The carbonyl groups increase electron affinity by lowering the pi density of the aromatic regions in the molecule.¹ The compound is especially useful for the addition of unsymmetrical imides, with one end able to contain the hydrophobic moiety used for LB film formation and the other able to contain the donor, which is connected to the perylene via a sigma bridge (**Figure 1.4.1**).⁹

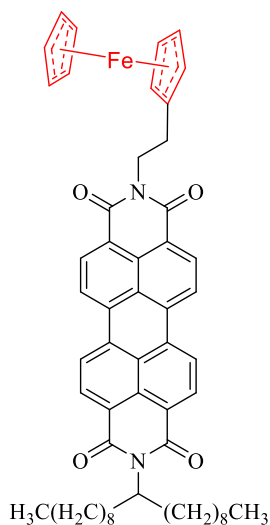


Figure 1.4.1: Example of D-σ-A molecule using a perylenebisimide acceptor and a ferrocene donor.³

The potential use of only the perylenebisimide acceptor in molecular rectification is also worth studying and is the subject of the following discussion. An acceptor alone can, theoretically, exhibit asymmetric rectification if it is placed asymmetrically in the electrode gap,

or closer to one electrode than to the other, as discussed above. It is possible that some D- σ -A rectifiers are following the asymmetric model, and that the donor portion is not even needed. To test that idea, we need a PBI acceptor with a long hydrophobic tail and a short hydrophilic tail, to fit asymmetrically between the electrodes. For successful LB film formation, a hydrophobic tail is needed at one end of perylene tetracarboxylic dianhydride (PTCDA) and a hydrophilic group at the other end. Long hydrocarbon chains attached in their middles, called swallowtails, are often used due to their high hydrophobicity and to increase the solubility of the perylenebisimides.⁴ For unidirectional molecular alignment in the LB trough, a hydrophilic group needs to be attached to the end of the PMA that opposes the swallowtail. This hydrophilic group should go into the water, while the swallowtail should face upward and out of the water.

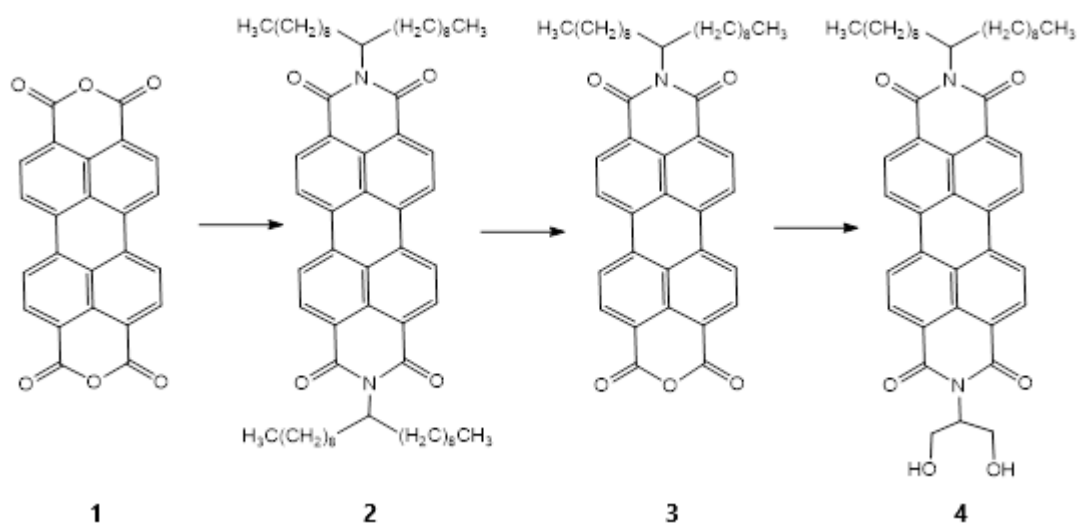


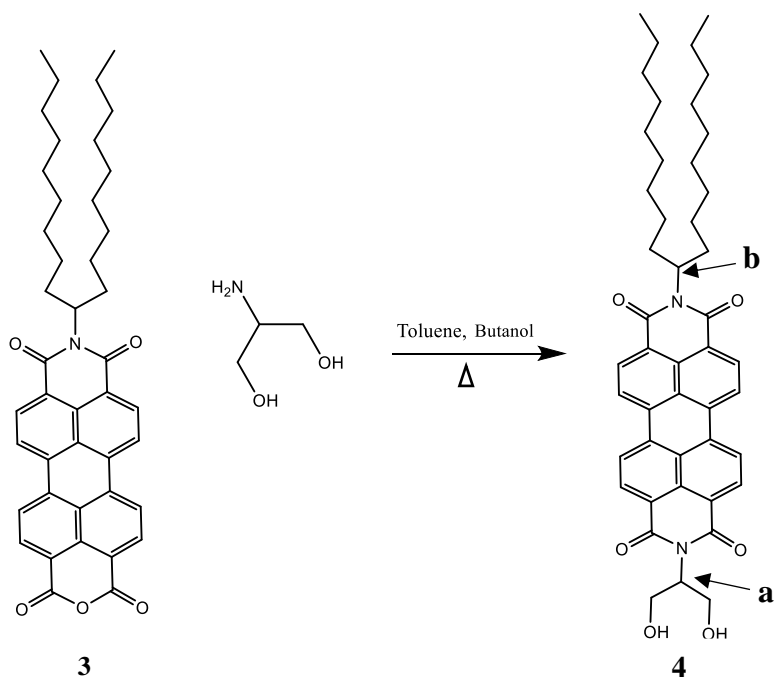
Figure 1.4.2: Synthesis of perylenebisimide with serinol and nonadecyl-swallowtail imides.

To test these hypotheses, the following experiments aimed to attach the hydrophilic compound serinol and the hydrophobic nonadecyl swallowtail to PTCDA to synthesize a perylenebisimide acceptor (**4**) (**Figure 1.4.2**). Previous reactions were conducted that successfully attached the hydrocarbon swallowtail to PTCDA (**1**), first resulting in a di-

swallowtail perylenebisimide intermediate (= PBI, **2**), which was then hydrolyzed in basic conditions to yield a mono-swallowtail perylene imide anhydride (= Perylene Mono Anhydride or PMA, **3**).³ Furthermore, the swallowtail itself was formed from the conversion of 10-nonadecanone to the ketoxime, which was then reduced to the amine.³ Oximes, so named from the combination of “oxygen” and “imine”, can be formed from reactions between ketones and hydroxylamine. PMA had been obtained prior to the following discussion, so its synthesis will not be further discussed.

2. Results and Discussion

2.1 Attempted Synthesis of *N*-(10-Nonadecyl)-*N'*-(1,3-dihydroxypropan-2-yl)perylene-3,4,9,10- bis(dicarboximide)



Scheme 1: Addition of 2-amino-1,3-propanediol to PMA.

This experiment aimed to react serinol with PMA to form *N*-(10-nonadecyl)-*N'*-(1,3-dihydroxypropan-2-yl)perylene-3,4,9,10- bis(dicarboximide), **4**.⁹ As previously discussed, the PMA used in this procedure, **3**, was previously created by refluxing perylene-3,4,9,10-tetracarboxylic dianhydride and a hydrocarbon swallowtailed amine, followed by semihydrolysis. Once the perylene was successfully mono-alkylated, it was refluxed with serinol (2-amino-1,3-propanediol). The reaction theoretically proceeds via acyl substitution, with the lone pair of the nitrogen in serinol attacking one of the anhydride carbonyl carbons on PMA. Reformation of C=O then causes the ring to break, and repetition of steps with nitrogen and the other carbonyl results in the unsymmetrical PBI **4** and water. A ¹H-NMR of the resulting product revealed the expected peaks, along with two peaks of unknown origin (5.79 ppm; 5.01 ppm), both of which were related by using COSY (**Figure 2.1.1**).

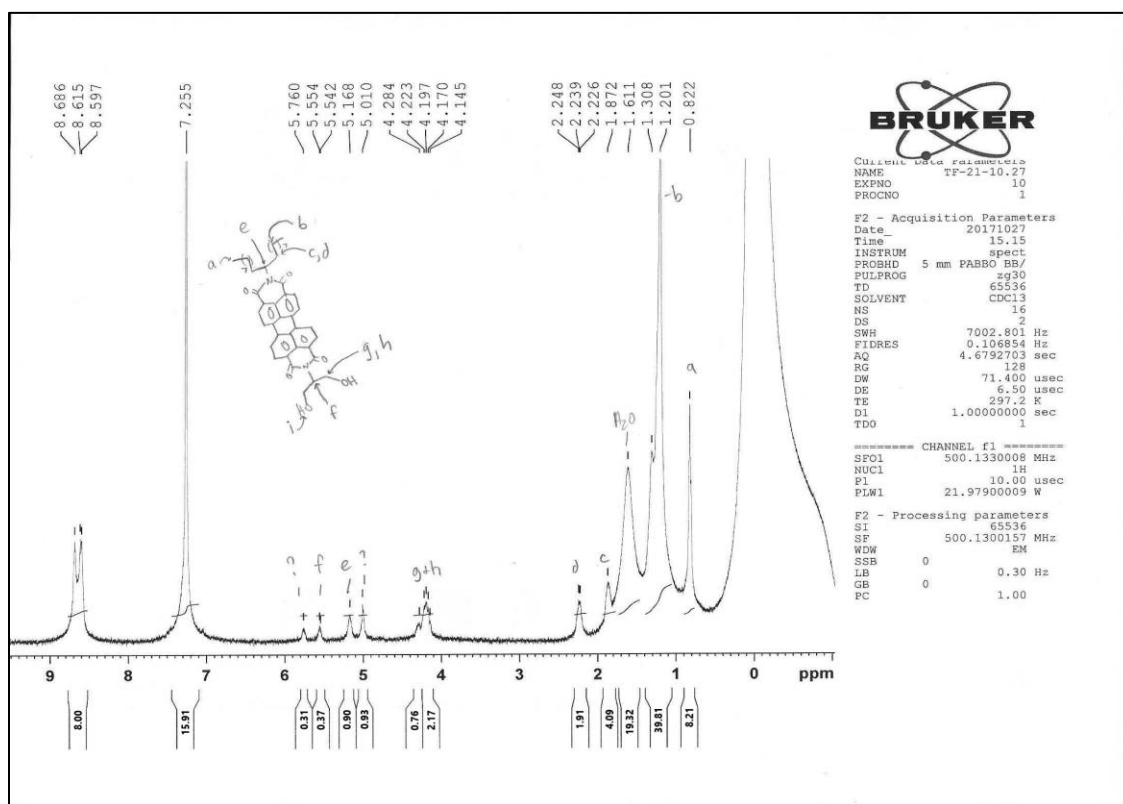


Figure 2.1.1: ¹H-NMR of supposed perylenebisimide.

Correlation spectroscopy (COSY), a type of two-dimensional NMR, is used to show the coupling patterns between hydrogens. According to the spectrum, the two unknown peaks were coupled to each other but were not coupled to any other hydrogens (**Figure 2.1.2**). Since they had similar chemical shifts as the peaks for the hydrogens of the secondary carbons bonded to nitrogen (**a**: 5.62 ppm; **b**: 5.17 ppm), a possible explanation for their appearance could be the presence of intramolecular interactions (**Scheme 1**).

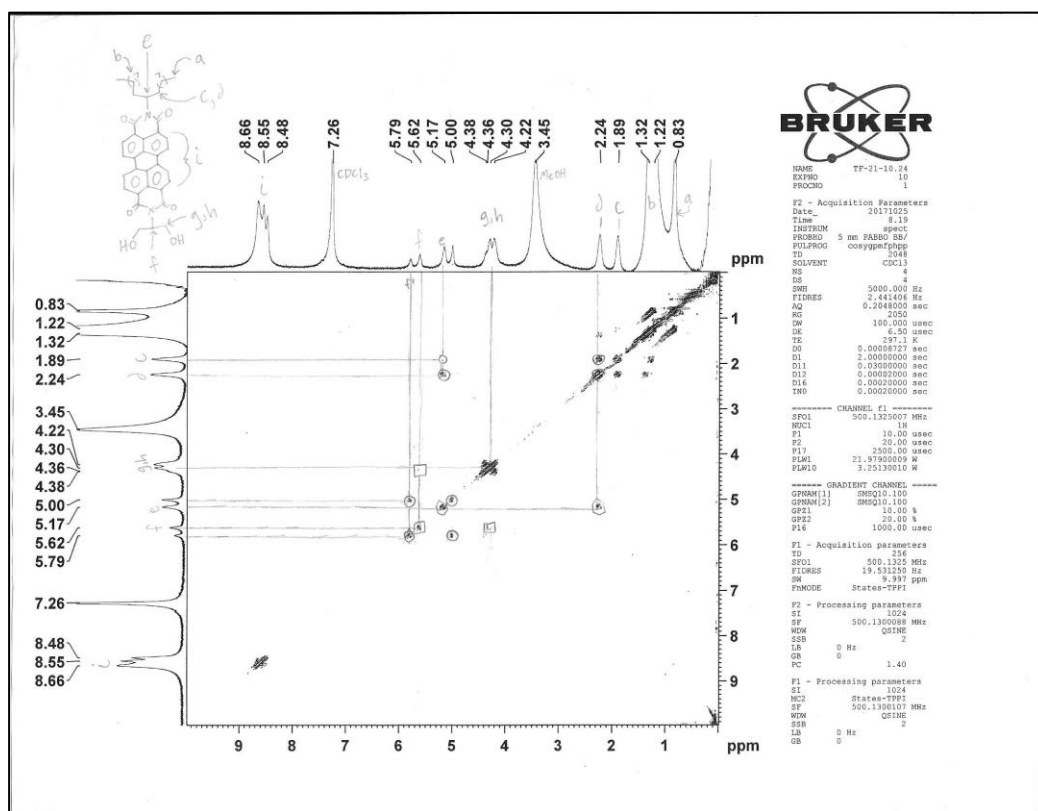


Figure 2.1.2: COSY spectrum of supposed perylenebisimide.

These unknown peaks could, therefore, be caused by the inductive effects from the oxygens in serinol, which could result in different chemical shifts depending on the orientation of the oxygens relative to the hydrogen attached to the secondary carbon (**a**) and the resulting magnitude of polarization the oxygen causes on that hydrogen. Also, it is possible that

intramolecular hydrogen bonding is occurring between the hydroxyl groups of serinol, resulting in a six-membered ring-like structure (**Figure 2.1.3**). Therefore, the orientation of the ring could be responsible for such peak complexities, since the hydrogens can be in either the axial or equatorial position. However, if the unknown peaks were, in fact, representing the same hydrogens as **a**, they should have been shown to couple the same neighboring hydrogens in the COSY spectrum.

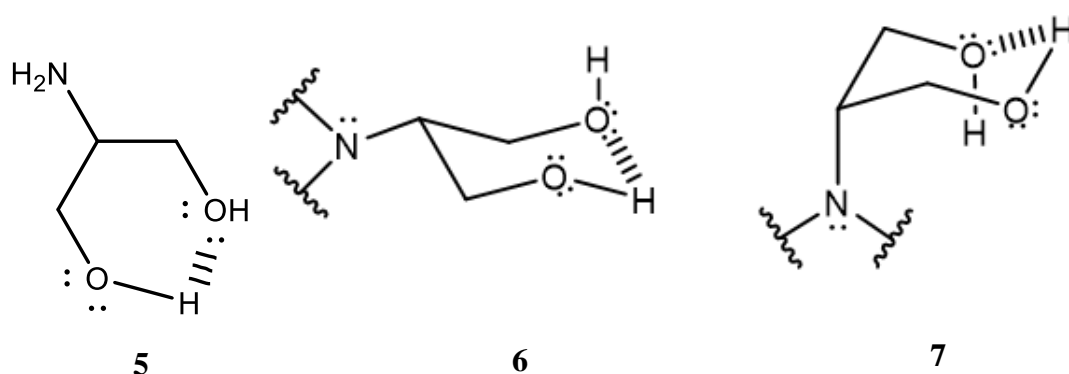
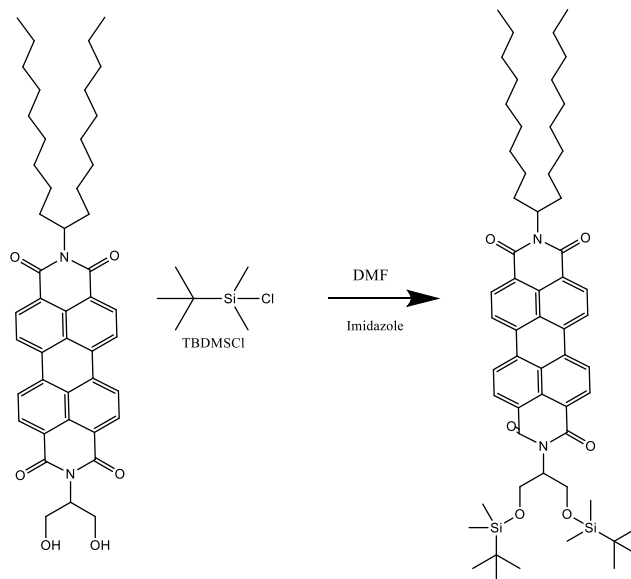


Figure 2.1.3: Potential intramolecular interactions between hydroxyl groups of serinol.

Furthermore, despite purification via column chromatography, the integrations of most of the expected peaks were lower than they should have been. For example, **a** represents 1 hydrogen, yet its integration was 0.37 (**Figure 2.1.1**). Since the product was purified, the presence of intramolecular interactions could also explain these unusual integration patterns and even the complex multiplicities observed in the spectra. For example, the axial and equatorial hydrogens attached to the secondary carbon in **6** and **7**, respectively, could have different chemical shifts and, consequently, different integrations due to their multiple possible orientations. So, due to these complexities and the inability to propose a confident explanation and also to be certain that the unidentified peaks were not impurities and that the serinol had been successfully attached to PMA, the following reactions were conducted to protect the

hydroxyl groups of serinol to prevent potential intramolecular interactions between the hydroxyl groups and PBI.

2.2 Protection of Proposed Perylenebisimide Hydroxyl Groups with TBDMSCl

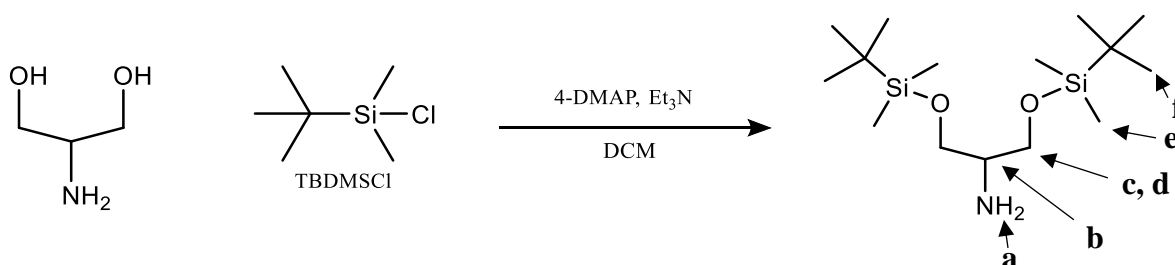


Scheme 2: Addition of TBDMSCl to hydroxyl groups of PBI.

The compound *tert*-butyldimethylsilyl chloride (TBDMSCl) was used in an attempt to protect the hydroxyl groups of the previously synthesized perylenebisimide in order to conclude whether or not the desired PBI was actually synthesized or if impurities or intramolecular orientation were responsible for the additional peaks in the ^1H -NMR of the previous reaction (**Scheme 1**). Upon completion of the reaction, the ^1H -NMR taken revealed some apparent product formation but mostly contained unidentified impurities and ultimately inconclusive results. Based on this spectrum, byproducts, such as *tert*-butyl(methoxy)dimethylsilane, were most likely produced, as well as mono-protected intermediates. The low percent yield (14.8%) can be explained by the multiple extractions and successive washes performed to remove

residual DMF. Solubility was also an issue because all of the perylenebisimide did not dissolve in the ethyl acetate extraction used to remove residual DMF, and an aggregate consequently formed between organic and aqueous layers. As a result of these difficulties, attempts were made to protect serinol prior to its addition to PMA.

2.3 Protection of 2-amino-1,3-propanediol using TBDMSCl

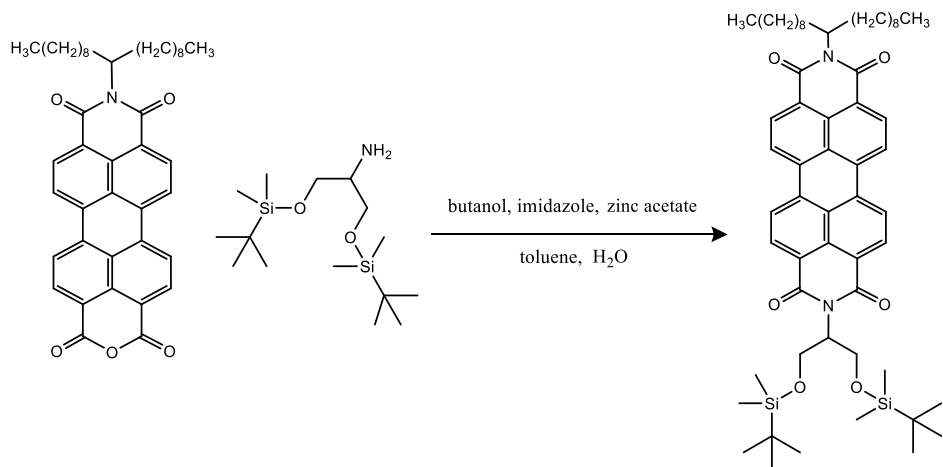


Scheme 3: Addition of TBDMSCl to serinol hydroxyl groups.

To avoid byproducts and unintended reactions, serinol alone was reacted with TBDMSCl in order to protect serinol's hydroxyl groups. The product was successfully obtained by Joana Salto, et al., from whom this procedure was taken.¹⁰ The reaction occurs when a lone pair of electrons on the oxygen of serinol attacks, or forms a bond with, Si of TBDMSCl. The chloride atom then leaves, resulting in a protected intermediate. Since both oxygens needed to be protected, 2.57 eq. of TBDMSCl were used. After multiple purification steps, the di-protected serinol was isolated (Yield: 1.12 g; 31.9%). The resulting low percent yield can be explained by the presence and consequent removal of tri-protected serinol and potentially unreacted material, along with losses during purification via column chromatography. ¹H-NMR data supported successful isolation, showing only expected peaks and unevaporated hexane. As expected, **a** presented a singlet at 1.92 ppm, **b** presented a quintet at 2.88 ppm, **c** and **d** presented two multiplets at 3.51 and 3.60 ppm, **f** presented a singlet at 0.89 ppm, and **e** presented a singlet at 0.046 ppm (**Scheme 3**). Each peak's integration was mostly within 0.20 of the expected values.

f's slightly high integration of 18.6 is likely due to overlap between product and hexane peaks. With successfully obtained TBDMS-protected serinol, attempts were made to react the product with PMA.

2.4 Addition of TBDMS-protected Serinol to PMA



Scheme 4: Proposed addition of TBDMS-protected 2-amino-1,3-propanediol to PMA.

TBDMS-protected serinol was reacted with PMA to produce a TBDMS-protected perylenebisimide. The reaction was run to completion and purified via column chromatography. However, though the results from the ^1H -NMR showed product formation, it also showed multiple unknown impurities, despite purification efforts. Possible explanations include starting with impure PMA material that contained both PTCDA and dialkylated perylenebisimide, as well as PMA, which was discovered due to three TLC spots in the starting material. Though the materials were separated via column chromatography after reacting with TBDMSCl , all products showed excessively large integrations for the hydrocarbon swallowtails and even showed some starting material peaks (**c**, **d**) on the ^1H -NMRs.

Therefore, the reaction was rerun with pure PMA, and three products identified by TLC were separated via column chromatography. ^1H -NMRs of the products with the two highest retention factors revealed similar peaks to the previous run and also appeared to contain some starting material (**c**, **d**). However, the integrations for the hydrocarbon swallowtail and TBDMS hydrogens were much more reasonable, yet still slightly higher than expected. Furthermore, those integrations for both products were very similar, which could indicate potentially different orientations of the same product. Since the molecule is not planar, perhaps the TBDMS-protected serinol and the swallowtail are either both oriented in the same direction outward from the aromatic region (*cis* isomer, **8**) or in the opposite direction (*trans* isomer, **9**) (**Figure 2.4.1**). The *cis* isomer would expose the aromatic region of the PBI and make it more likely to associate with the silica gel, causing a lower R_f . The aromatic region of the *trans* isomer, however, would not be as exposed, so the molecule would have a higher R_f . Further analysis is required to confirm that these two products are the same, however, before this hypothesis can be supported.

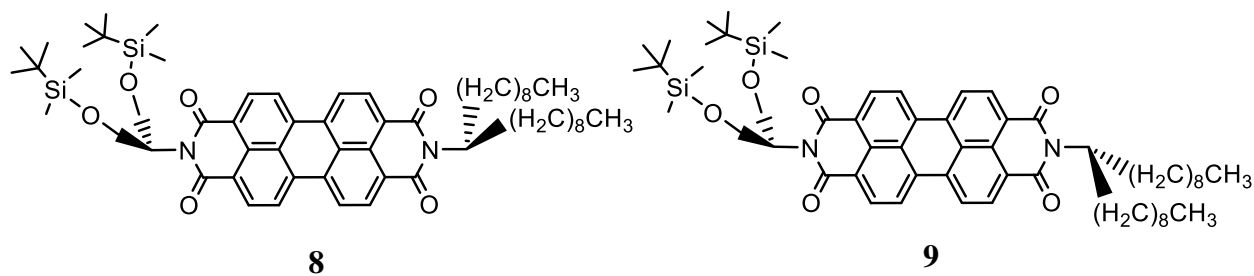
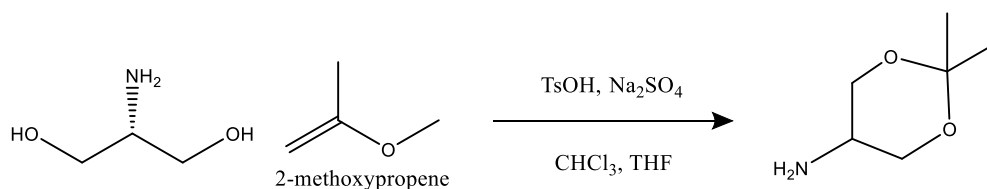


Figure 2.4.1: Possible orientations of TBDMS-protected PBI.

Since the integrations, specifically of the TBDMS hydrogens, are very similar between the two products, it is unlikely that the product with the lower R_f is a mono-protected PBI. Additionally, the third product with the lowest R_f was insoluble in the eluting solvent used for purification, along with several other solvents like DCM, and was finally removed with 95:4:1 CHCl_3 :MeOH:TFA. Its ^1H -NMR revealed many impurities and no product formation.

hydroxyl group oxygens then forms a bond with the carbocation. The methoxy group leaves, and the reaction steps repeat for the other hydroxyl group, resulting in the product.

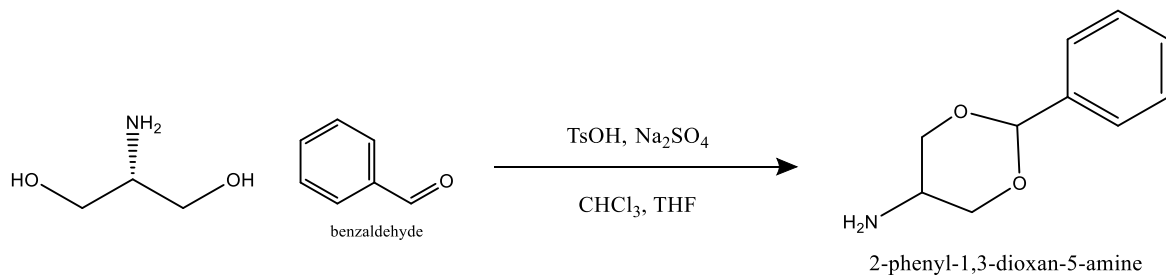
Unfortunately, the reaction was worked up before TLC showed completion, but the $^1\text{H-NMR}$ showed some product formation, along with multiple byproducts and possibly intermediates. The reaction was then run a second time but did not work. Possible explanations include stir plate malfunction and misread TLC plates. Another possibility is that in this second reaction, TsOH was used instead of camphorsulfonic acid, which was used in the literature and in the previous reaction. However, this substitution is a very unlikely cause. It is possible that the reaction again did not run to completion, but this time, no product was formed based on $^1\text{H-NMR}$ spectra of the organic layer following extraction. As a result, a second method for protecting serinol with 2-methoxypropene was pursued.



Scheme 6: Potential alternate reaction for protecting serinol using 2-methoxypropene.

A procedure that originally used benzaldehyde to protect serinol, which is described in the next experiment, was used with 2-methoxypropene instead to form 2,2-dimethyl-[1,3]dioxan-5-ylamine.¹² The reaction mechanism is similar to the previous one. Additional TsOH (slightly over 3 eq.) was added to aid reaction completion but was insoluble in the reaction mixture. Though TLC showed the disappearance of starting material, no clear product spot appeared. Likewise, $^1\text{H-NMR}$ spectra did not show successful product formation.

2.6 Preparation of 2-phenyl-1,3-dioxan-5-amine



Scheme 7: Protection of serinol using benzaldehyde.

Serinol was reacted with benzaldehyde to produce a cyclic product that protects the hydroxyl groups of serinol and that could, therefore, prevent intramolecular interactions when reacted with PMA. This reaction, taken from Lanrong Bi, et al., begins with protonation of the amino group in serinol due to the addition of TsOH.¹² It then proceeds through a hemiacetal intermediate, with the loss of water, before resulting in the cyclized product shown above. Sodium sulfate was used to remove the water and, consequently, to push the reaction towards product formation. When the reaction did not seem to be progressing, more TsOH was added, which was insoluble in the mixture, despite heating. TLC showed disappearance of starting material but no clear product spot, and the benzaldehyde spot did not disappear. Likewise, ¹H-NMR data showed benzaldehyde and THF but no product. One possible explanation could be that the amino group on serinol reacted with benzaldehyde, forming an imine. Therefore, reactions to protect the amino group prior to reacting it with benzaldehyde should be pursued.

3. Future Work

Further pursuit of obtaining a cyclic-protected product, such as 2-phenyl-1,3-dioxan-5-amine, is worth pursuing in future experiments. Such a cyclic compound would prevent hydrogen bonding between the hydroxyl groups of serinol, and its synthesis would require only around one equivalent of the protecting group relative to serinol. After the addition of the protected serinol to the PMA, the resulting PBI (**11**) would give insight to the complexities in ^1H -NMR spectra while also confirming whether or not the PBI can be synthesized by using unprotected serinol (**Figure 3.1.1**). Additionally, using 2-methoxypropene as a protecting group should also be further explored. If such a protected serinol was obtained, its addition to PMA would yield **10**. Furthermore, the products obtained from the addition of TBDMS-protected serinol to PMA, specifically the successfully isolated product with the highest R_f , retain their potential to yield the PBI and should be further purified and analyzed.

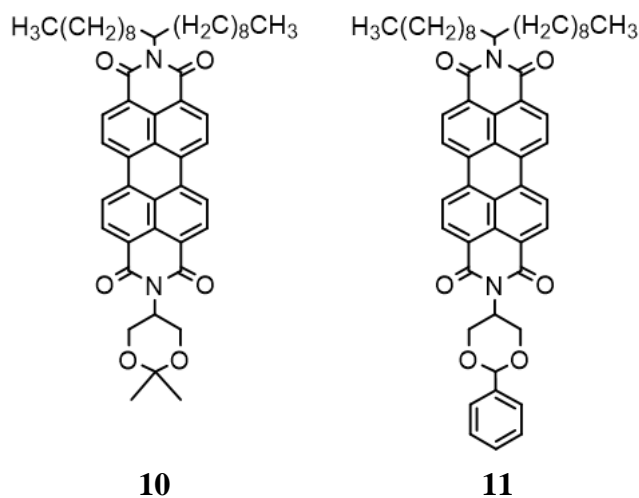


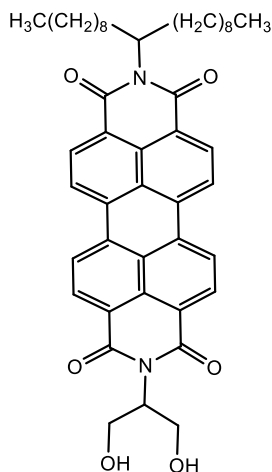
Figure 3.1.1: Proposed cyclic-protected PBI. Theoretically, subsequent removal of the protecting group would yield the desired PBI acceptor.

4. Conclusion

Attempts to synthesize *N*-(10-Nonadecyl)-*N'*-(1,3-dihydroxypropan-2-yl)perylene-3,4,9,10- bis(dicarboximide), though potentially unsuccessful, showed yet again that seemingly simple reactions are often more complex than they appear due to the presence of intramolecular interactions and non-planar molecules. Though this research failed to produce an acceptor molecule useful in molecular rectification, it has given direction to further research. Methods to protect the hydroxyl groups of serinol must be explored and pursued before it can be reacted with PMA, so that the synthesis of the PBI can be confirmed and the complexities observed in NMR spectra explained. As previously seen, it is important to find a reaction where the protecting group does not also react with the amino group, as in the reaction depicted in **Scheme 3** where tri-protected serinol was produced and lost, as a result. Nevertheless, the synthesized TBDMS-protected PBI could very well lead to the desired acceptor if the TBDMS groups can be successfully removed. In conclusion, the potential of *N*-(10-Nonadecyl)-*N'*-(1,3-dihydroxypropan-2-yl)perylene-3,4,9,10- bis(dicarboximide) in molecular rectification remains unknown but, nevertheless, holds promise for future research.

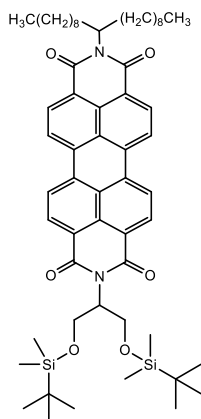
5. Experimental

***N*-(10-Nonadecyl)-*N'*-(1,3-dihydroxypropan-2-yl)perylene-3,4,9,10-bis(dicarboximide) (TF-64)**



Perylene-3,4,9,10-tetracarboxylic dianhydride (100 mg; 4.0 mmol), serinol (42.5 mg; 456 μ mol; 3 eq.), butanol (15 mL), and toluene (15 mL) were combined in a 50 mL round bottom flask and heated under reflux to 105°C for 20 hours. The product was vacuum filtrated and washed with MeOH. (Yield: 99.0 mg; 89%) The product (63.4 mg) was then purified via column chromatography using enough 9:1 CHCl_3 : CF_3COOH to initially dissolve it, and 94:5:1 CHCl_3 :MeOH: CF_3COOH was used as the eluent. The desired fractions were concentrated using rotary evaporation. ^1H -NMR yielded various complexities, as discussed above. (Yield: 7.00 mg; 0.24%).

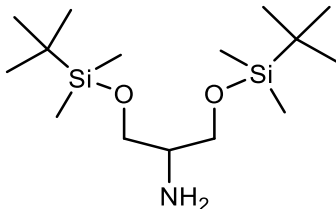
TBDMS-protected PBI (TF-67)



Perylenebisimide (66.4 mg; 90.8 μ mol), imidazole (32.0 mg; 470 μ mol), TBDMSCl (37.0 mg; 245 μ mol), and DMF (6.00 mL) were combined and stirred at r.t. Additional DMF (5.5 mL) was added after 69 h to help stimulate product formation. After an additional 24 h, 19.5 mg of TBDMSCl and 13.8 mg of imidazole were added, and the temperature was increased to 39°C. The reaction mixture was then removed from heat after another 48 h. Hexane (66.0 mL) and sat. aq. ammonium chloride (22.0 mL) were used to wash the mixture, followed by four additional washes. Residual DMF was present in the product, so the product was partitioned between 40.0 mL of ethyl acetate and 20.0 mL of 1:1 aq. NH_4Cl and the organic layer was washed with 15.0 mL of 1:1 aq. sat. NH_4Cl five times. The mass of the product soluble in ethyl acetate was 12.9 mg (Yield: 14.8%). Pinkish aggregates in the aqueous acid layer suggested perylenebisimide that was insoluble in ethyl acetate. As a result, the insoluble perylenebisimide in the aqueous layer was partitioned between DCM and aq. sat. 1:1 NH_4Cl . The organic layer was then washed 3 times with 1:1 aq. sat. NH_4Cl , dried with magnesium sulfate, and concentrated using rotary evaporation. (Yield: 2.50 mg; 2.87%) The ^1H -NMR spectrum, though showing possible product formation, revealed an abundance of potential byproducts and impurities. TLC's of samples taken on successive days during the reaction originally showed

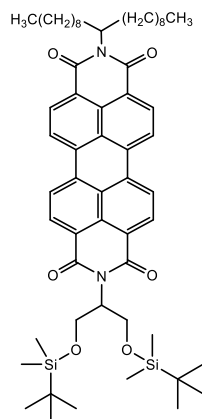
partial product formation (2 spots present) but then later showed only one spot with the same Rf as the starting material.

TBDMS-protected Serinol (TF-68) 2,2,3,3,9,9,10,10-octamethyl-4,8-dioxa-3,9-disilaundecan-6-amine



Serinol (1.01 g; 11.0 mmol), DMAP (6.50 mg; 51.1 μ mol), and DCM (12.5 mL) were combined under argon, and 6.0 mL of triethylamine was added. After 1 hr., TBDMSCl (4.25 g; 28.2 mmol) and DCM (6.25 mL) were combined in a second flask and then added. The reaction was held at r.t. and stirred overnight. An additional 18.75 mL of DCM was added for the extraction, and the organic layer was washed thrice with 12.5 mL of H₂O, dried, and concentrated via rotary evaporation, yielding a crude mass of 3.61 g (Yield: 103%). The crude product was then purified twice using flash chromatography with 95:5 hexane:ethyl acetate. (Yield: 1.12 g; 31.9%). ¹H NMR (300 MHz, CDCl₃) δ 3.597, 3.507 (AB part of ABX system, J_{AB} = 9.6 Hz, J_{AX} = 5.1 Hz, J_{BX} = 5.7 Hz, 2H each), 2.877 (quint., J = 5.4 Hz, 1H), 1.918 (s, 2H), 0.885 (s, 18H), 0.046 (s, 12H) ppm.

TBDMS-protected PBI (TF-70)

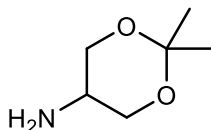


PMA (108 mg; 0.164 mmol), TBDMS-protected serinol (148 mg; 0.463 mmol), and toluene (21 mL) were refluxed at 105°C for 24 hrs. Additional TBDMS-protected serinol (81.4 mg) in toluene (4 mL) was added, equaling 4.36 eq. total TBDMS-protected serinol added. At 9 days, the temperature was increased to 116°C, and at 34 days, 1-butanol (2.5 mL) was added. At 43 days, imidazole (319 mg; 4.69 mmol) was added. At 44 days, dihydrated zinc acetate (28.7 mg) was added as a catalyst, and the temperature was raised to 122°C. At 45 days, the reaction was extracted multiple times, dried, and concentrated via rotary evaporation (Yield: 91.4 mg; 58.0%). The product was then purified using column chromatography (Yield: 66.1 mg; 41.9%). ¹H-NMR showed some product formation but mostly impurities. It was subsequently determined by TLC that the starting PMA was impure, so the reaction was repeated with pure PMA.

PMA (50.9 mg; 77.4 μmol) and TBDMS-protected serinol (81.5 mg; 255 μmol) were combined in toluene (12 mL) and were refluxed at 78.5 °C for 23 hrs. Zinc acetate (19.6 mg) was then added as a catalyst. After an additional 25 hrs., only partial product formation had occurred, as indicated by TLC, so imidazole (154.5 mg) was added. After another additional 24

hrs., the temperature was increased to 107 °C. After 23 hrs., TLC showed the disappearance of starting material, so the reaction mixture was allowed to come to room temperature. The product was then extracted with DCM, washed with water, and dried to yield a crude mass of 175 mg. Three spots indicated by TLC were isolated using column chromatography (7:3 hexane: ethyl acetate). The product with the lowest R_f was insoluble in the eluting solvent and was removed with 95:4:1 CHCl₃:MeOH:TFA. To remove TFA, the product was then extracted with CHCl₃ and 5% aq. NaHCO₃, dried, and concentrated with rotary evaporation. Masses of the products from highest R_f to lowest were 39.5 mg (53.21 %), 19.6 mg (26.4 %), and 3.6 mg (4.85 %), respectively. ¹H-NMRs were taken for all three products but only revealed product formation in the two products with the highest retention factors, whose spectra also revealed the potential presence of starting material, along with higher integrations than expected. In an attempt to remove possible starting material, some of the product with the lower of the two retention factors was extracted with DCM and aq. HCl at a pH of ~5. However, the resulting ¹H-NMR revealed no change. The product with the highest R_f was then isolated a second time via column chromatography to yield a pure TBDMS-protected PBI. ¹H NMR (400 MHz, CDCl₃) δ 8.51 – 8.61 (m, 8H), 5.48 (quint., *J* = 8 Hz, 1H), 5.18 (quint., *J* = 4 Hz, 1H), 4.19 – 4.21 (m, 4H), 2.26 (m, 2H), 1.88 (m, 2H), 1.20 (s, 28H), 0.82 (s, 6H), 0.80 (s, 18H), 0.05 (s, 12H) ppm. ¹³C NMR (400 MHz, CDCl₃) δ 165.08, 164.35, 163.96, 134.88, 132.27, 131.76, 129.84, 126.78, 123.93, 123.36, 61.33, 58.14, 55.13, 32.71, 32.20, 29.88, 29.61, 27.32, 26.10, 22.99, 18.46, 14.43, -5.05 ppm. IR (neat): 2925, 2854, 1700, 1656, 1593, 1401, 1336, 1250, 1080, 834, 807, 775, 737.

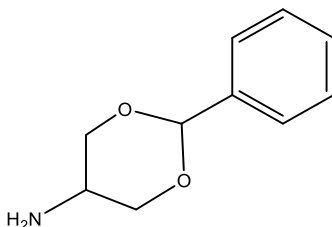
2,2-Dimethyl-[1,3]dioxan-5-ylamine (TF-69; TF-75)



Procedure 1 (TF-69): Serinol (4.55 g; 50.0 mmol) was dissolved in 35.0 mL of DCM and placed in an ice water bath under argon.¹¹ Camphorsulfonic acid (12.8 g; 55.0 mmol) was then added, and the mixture was stirred for 5 minutes. 2-Methoxypropene (7.14 mL) was added dropwise over 35 minutes. The reaction mixture was then taken off of the water bath and allowed to come to r.t. The mixture was then stirred at r.t. for 19.5 hours and then slowly poured into cold 10% aq. NaOH and stirred. Brine was then added, and the layers were separated. The organic layer was washed again with the same agents, dried, and concentrated via rotary evaporation (Yield: 0.608 g; 9.28%). ¹H-NMR indicated some product formation, as well as unidentified peaks.

Procedure 2 (TF-75): Serinol (183 mg; 2.0 mmol), 2-methoxypropene (197 mg; 2.60 mmol), chloroform (50 mL), TsOH (30.3 mg), sodium sulfate (108 mg), and THF (4 mL) were combined and stirred at r. t. for 2 days.¹² Additional TsOH (349 mg) (2.20 mmol total) was added, and after 3 additional days, the reaction mixture was heated to try to dissolve precipitated TsOH, which did not dissolve after said heating. According to TLC, starting material was gone after 1 additional day, so sodium carbonate was added to bring the pH to 7. The product was then filtered and concentrated via rotary evaporation to yield a crude mass of 970 mg. ¹H-NMR spectra showed unsuccessful product formation.

2-Phenyl-1,3-dioxan-5-amine (TF-74)



Serinol (183 mg; 2.0 mmol), benzaldehyde (284 mg; 2.60 mmol), chloroform (50 mL), TsOH (32.4 mg), sodium sulfate (101 mg), and THF (4 mL) were combined and stirred at r. t. for 2 days.¹² Additional TsOH (346 mg) (2.20 mmol total) was added, and after 3 days, the reaction mixture was heated to dissolve precipitated TsOH, which did not dissolve after heating. After 1 additional day, TLC showed the disappearance of starting material, so sodium carbonate was added to bring the pH to 7. The solution was then filtered and concentrated via rotary evaporation to yield a crude mass of 400 mg. ¹H-NMR spectra show unsuccessful product formation.

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